PCT/GB03/00163

Rec'd PCT/PTO 16 JUL 2004

INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

REC'D 07 MAR 2003
WIPO PCT

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed Stephen Hordley

Dated 4 February 2003

Patents Form 1/77

Patents Act 1977
(Rule 16)

1/77

21JAN02 E689111-4 D02246
P01/7700 0.00-0201141.9

THE PATENT OFFICE
H
18 JAN 2002
LONDON

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

P013264GB NJN

2. Patent application number
(The Patent Office will fill in this part)

0201141.9

18 JAN 2002

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

I.C. Innovations Limited
47 Prince's Gate
Exhibition Road
London, SW7 2QA

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

7952369001

4. Title of the invention

COORDINATION COMPLEX

5. Name of your agent *(if you have one)*

D Young & Co

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

21 New Fetter Lane
London
EC4A 1DA

Patents ADP number *(if you know it)*

59006

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes

tents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	0
Description	16
Claim *(s)*	7
Abstract	1
Drawing *(s)*	2 +2

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature [signature] Date 18 January 2002

D Young & Co (Agents for the Applicants)

12. Name and daytime telephone number of person to contact in the United Kingdom — Neil Nachshen — 020 7353 4343

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.*

b) *Write your answers in capital letters using black ink or you may type them.*

c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*

d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*

e) *Once you have filled in the form you must remember to sign and date it.*

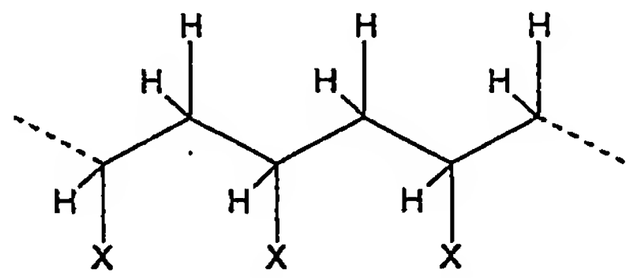
f) *For details of the fee and ways to pay please contact the Patent Office.*

COORDINATION COMPLEX

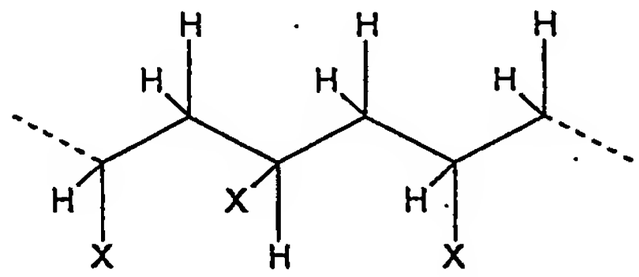
The present invention relates to a series of discrete, well-defined coordination complexes. More specifically, the invention concerns the use of Group 2 metal complexes in the controlled polymerisation of acrylate and alkylmethacrylate monomers.

Over recent years, an important technological objective has been the controlled, 'living' polymerisation of acrylate and alkylmethacrylate monomers to give products of controlled molecular weight and molecular weight distribution, and to provide access to block co-polymer materials. Examples of controlled or 'living' polymerisations include anionic polymerisation [C. Zune, R. Jérôme, Prog. Polym. Sci., 1999, 24, 631], group transfer polymerisation [O.W. Webster, W.R. Hertler, D.Y. Sogah, W.B. Farnham, T.V. Rajanbabu, J. Am. Chem. Soc., 1983, 105, 5706], atom transfer radical polymerisation [K. Matyjaszewski, J. Xia, Chem. Rev., 2001, 101, 2921], immortal polymerisation [T. Aida, S. Inoue, Acc. Chem. Res., 1996, 29, 39], catalytic chain transfer polymerisation [T.P. Davis, D.M. Haddleton, S.N. Richards, J. Macromol. Sci. Rev. Macromol. Chem. Phys., 1994, C34, 243], screened anionic polymerisation [D.G.H. Ballard, R.J. Bowles, D.M. Haddleton, S.N. Richards, R. Sellens, D.L. Twose, Macromolecules, 1992, 25, 5907] and metal-free anionic polymerisations [M.T. Reetz, Angew. Chem., Int. Ed. Engl. 1988, 27, 994].

Stereospecific polymers can exist in two different forms, isotactic and syndiotactic, as shown below.



ISOTACTIC



SYNDIOTACTIC

By way of contrast, an atactic polymer is one that has no regular arrangement along the chain.

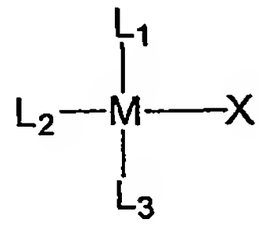
Another important objective in the field of polymer chemistry has been to develop systems that can control the tacticity of products such as polymethylmethacrylate under industrially relevant process conditions. For example, the higher softening temperature accompanying highly syndiotactic polymethylmethacrylate confers beneficial properties on the resultant materials. Examples include s-PMMA for injection molding, artificial marble pre-mixes, stereocomplexes for preparing membranes and/or gel base materials, and syndiotactic-isotactic block PMMA for forming resist patterns.

To date, a number of systems have been described that can effect syndiotactic control in polymethylmethacrylate. These include organolanthanides [H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake and A. Nakamura, J. Am. Chem. Soc., 1992, 114, 4908; M. Nodono, T. Tokimitsu, S. Tone, T. Makino and A. Yanogase, Macromol. Chem.. Phys., 2000, 201, 2282], zirconocenes [A.D. Bolig and E. Y.-X. Chen, J. Am. Chem. Soc., 2001, 123, 7943] aluminium compounds [T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto and K. Hatada, Makromol. Chem. Suppl., 1989, 15, 167; G.L.N. Péron, R.J. Peace and A.J. Holmes, J. Mater. Chem., 2001, 11, 2915], magnesium compounds [T.Kitayama, T.Shinozaki, E. Masuda, M. Yamamoto and K. Hatada, Polym. Bull., 1988, 20, 565] and enamine initiators [M. Miyamoto and S. Kanetaka, J. Polym. Sci.: Part A: Polym. Chem., 1999, 37, 3671]. Most of these systems are accompanied by one or more limitations: either exceptionally low temperatures (e.g. –78°C or below) are required to obtain high syndiotacticity, and/or the molecular weight control over the resultant product is poor.

The present invention thus seeks to provide a series of discrete, well-defined coordination complexes that are useful as initiators in the polymerisation of alkylacrylate and/or alkylmethacrylate monomers. More specifically, the invention seeks to provide coordination complexes that are capable of influencing and/or

controlling the syndiotacticity of the resulting polymer but which alleviate some of the above-mentioned problems associated with prior art complexes.

In a first aspect, the invention provides a complex of formula I



I

wherein

M is Ca, Mg, Ba or Sr;

L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P and substituted or unsubstituted cyclopentadienide, where R^{1-6} are each independently H or hydrocarbyl;

L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C{=}NR^9$, $PR^7R^8R^9$, or a heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3 may be the same or different to L_2; or L_3 is linked to a further metal centre; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, an aryl group, an aryloxide or an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein $R^{10\text{-}12}$ are each independently H or hydrocarbyl;

with the proviso that when L_1 and L_2 are $\{HC(C(CH_3){=}N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}$ and M is magnesium, X is other than Me or ^{t}Bu.

As used herein, the term "hydrocarbyl" refers to a group comprising at least C and H that may optionally comprise one or more other suitable substituents. Examples of such substituents may include halo-, alkoxy-, nitro-, an alkyl group, or a cyclic

group. In addition to the possibility of the substituents being a cyclic group, a combination of substituents may form a cyclic group. If the hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked via a suitable element or group. Thus, the hydrocarbyl group may contain heteroatoms. Suitable heteroatoms will be apparent to those skilled in the art and include, for instance, sulphur, nitrogen, oxygen, phosphorus and silicon.

~~Preferably, M is Ca or Mg.~~

In a preferred embodiment, R^1 and R^2 are hydrocarbyl, and R^{3-6} are H or hydrocarbyl.

In a particularly preferred embodiment, R^1 and R^2 are each independently selected from branched or unbranched alkyl, branched or unbranched alkenyl, or aryl, each of which may be substituted or unsubstituted.

As used herein, the term "alkyl" refers to a saturated carbon-containing chain which may be straight or branched, and substituted (mono- or poly-) or unsubstituted. Suitable substituents include those which do not have any significant adverse effect on the activity of the complex.

Preferably, the alkyl group is a C_{1-20} alkyl group, more preferably a C_{1-10} alkyl group.

Accordingly, the term "haloalkyl" refers to an alkyl group substituted by at least one halogen, for example, chlorine, bromine, fluorine or iodine.

Accordingly, the term "heteroalkyl" refers to an alkyl group containing at least one heteroatom, for example, O, N or S.

As used herein, the term "alkenyl" refers to a C_{2-20} unsaturated carbon-containing chain which may be branched or unbranched, and substituted (mono- or poly-) or unsubstituted. Preferably the alkenyl group is a C_{2-10} alkenyl group.

As used herein, the term "aryl" refers to a C_{6-10} aromatic, substituted (mono- or poly-) or unsubstituted. Again, suitable substituents include those which do not have any significant adverse effect on the activity of the complex.

As used herein, the term "cycloalkyl" refers to a cyclic alkyl group which may be substituted (mono- or poly-) or unsubstituted.

As used herein, the term "heterocycle" refers to an aromatic or non-aromatic heterocycle comprising one or more heteroatoms. Preferred heterocycle groups include pyrrole, pyrimidine, pyrazine, pyridine, quinoline, thiophene and furan.

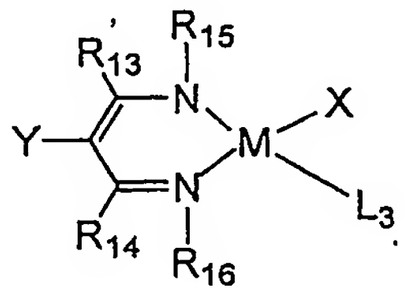
In one preferred embodiment, X is an alkyl group.

In another preferred embodiment, X is an enolate group of formula $R^{10}R^{11}C=CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl. Preferably, R^{10} and R^{11} are H and R^{12} is an aryl group.

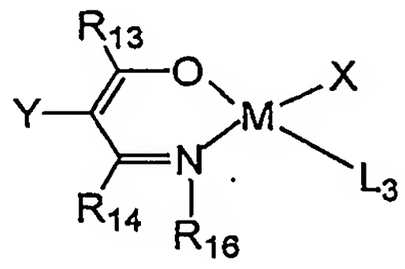
Even more preferably, X is ^{i}Pr or -OC $(=CH_2)Ar$, wherein Ar = 2,4,6,-$Me_3C_6H_2$.

In a preferred embodiment, L_1 and L_2 are linked to form a bidentate ligand selected from derivatives of acetylacetonate, e.g. a beta-diketiminate or a beta-ketoiminate.

In one preferred embodiment, the complex of the invention is of formula II or III



II



III

wherein

Y is H, halogen, NO_2, hydrocarbyl or CN;

R^{13-16} are each independently selected from H and hydrocarbyl; or Y and R^{13} are linked to form a hydrocarbyl group; and

L_3 is as defined above.

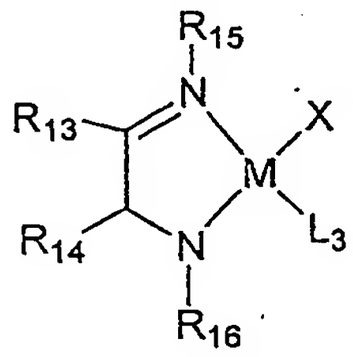
In a more preferred embodiment,

Y is selected from H, halogen, NO_2, CN, alkyl, aryl, haloalkyl or heteroalkyl;

R^{13-16} are each independently selected from alkyl, aryl, heteroalkyl, haloalkyl, cycloalkyl and a heterocyclic ring containing at least one O, N or S atom; or Y and R^{13} are linked to form an aryl group; and

L_3 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7C{=}NR^8$, $PR^7R^8R^9$, thiophene and tetrahydrofuran, where R^{7-9} are each independently H or a hydrocarbyl group.

In another preferred embodiment, the complex of the invention is of formula V



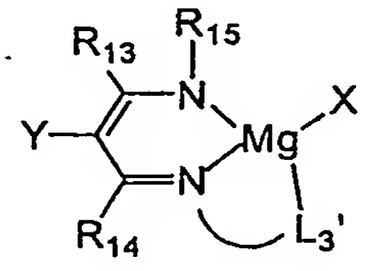
V

wherein R^{13-16} are as defined above, and where R^{13} and R^{15} are optionally linked to form an aryl group.

In one preferred embodiment of the invention, L_1, L_2 and L_3 are linked to form a tridentate ligand.

In a particularly preferred embodiment, L_1, L_2 and L_3 are linked to form a tridentate ligand selected from a beta-diketiminate with a pendant donor group, and a Schiff base derivative with a pendant donor arm.

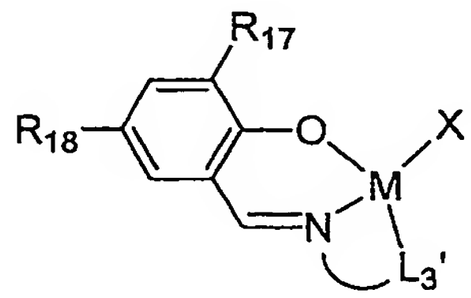
Even more preferably, the complex of the invention is of formula VI



VI

wherein L_3' is defined as for L_3 above, and is linked to the nitrogen of the bidentate ligand via a linker group.

In an alternative preferred embodiment, the complex is of formula VII

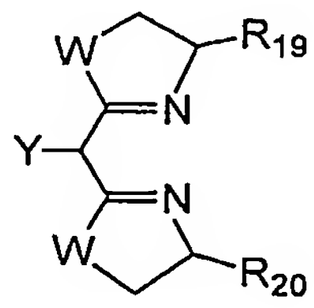


VII

wherein L_3' is defined as for L_3 above, and is linked to the nitrogen of the bidentate ligand via a linker group, and R^{17-18} are as as defined for R^{13-16} above .

Preferably, where the complex is of formula VI or VII, the linker group is $(CH_2)_n$ where n is 0-6, an arylene group, or SiR_2, where R is a hydrocarbyl group.

In yet another preferred embodiment of the invention, L_1 and L_2 form a bidentate ligand of formula VIII



VIII

wherein

Y is as defined above;

W is O, NH, NR' or CH_2, where R' is a hydrocarbyl group.; and

R^{19-20} are as defined for R^{13-16} above.

In one preferred embodiment, the invention comprises a dimer of a complex as described hereinbefore.

In an especially preferred embodiment, the complex of the invention is selected from the following:

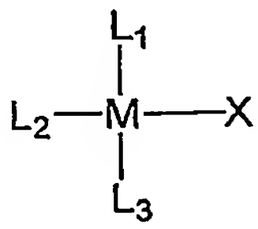
$\{HC(C(CH_3)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}Mg^iPr$;

$[\{HC(C(CH_3)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$;

$[\{HC(C(CH_3)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)\cdot Et_2O]$;

wherein Ar = 2,4,6,-$Me_3C_6H_2$.

In a second aspect, the invention relates to the use of a complex of formula Ia as a polymerisation initiator,



Ia

wherein

M is Ca, Mg, Ba or Sr;

L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P and substituted or unsubstituted cyclopentadienide, where R^{1-6} are each independently H or hydrocarbyl;

L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C{=}NR^9$, $PR^7R^8R^9$, or a heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3 may be the same or different to L_2; or L_3 is linked to a further metal centre; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, and aryl group, an amide, an alkoxide, an aryloxide or an enolate group of formula $R^{10}R^{11}C=CR^{12}O$-, wherein $R^{10\text{-}12}$ are each independently H or hydrocarbyl;

with the proviso that when L_1 and L_2 are $\{HC(C(CH_3)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}$, M is magnesium, X is other than Me or ^{t}Bu.

Preferably, M is Ca or Mg.

The preferred embodiments for the second aspect of the invention are identical to those described hereinabove for the first aspect.

In a preferred embodiment, the invention relates to the use of a complex of formula Ia in the polymerisation of acrylate and/or alkylacrylate monomers. In particular, the complexes of the present invention are capable of influencing the tacticity of the resulting polymer. More specifically, the complexes of the invention are capable of inducing a high degree of syndiotacticity in the resulting polymer.

As used herein, the term "acrylate monomer" refers to an acrylate monomer which is optionally substituted by one or more hydrocarbyl groups as defined hereinabove.

Similarly, the term "alkylacrylate" refers to an alkylacrylate monomer which is optionally substituted by one or more hydrocarbyl groups as defined hereinabove.

Preferably, said acrylate and alkylacrylate monomers are substituted by branched acyclic and cyclic hydrocarbons and/or functionalised substituents such as hydroxyalkyl, glycidyl and glycolethers.

Preferably, said acrylate monomer is an alkylacrylate.

Preferably, said alkylacrylate monomer is an alkylmethacrylate.

One preferred embodiment relates to the use of complexes in accordance with the second aspect of the invention as initiators in the preparation of block copolymers. By way of example, said complexes may be used in the preparation of a block copolymer of methyl methacrylate and n-butyl methacrylate. Further details of this aspect of the invention are provided in the accompanying examples section.

In a third aspect, the invention provides a process for the polymerisation of acrylate and/or alkylacrylate monomers, said process comprising contacting an initiating amount of a complex of formula Ia as defined above with an acrylate and/or an alkylacrylate monomer in the presence of a suitable solvent.

In a preferred embodiment, the invention provides a polymerisation process for preparing a block copolymer, for example, a block copolymer of methyl methacrylate and n-butyl methacrylate.

In a further preferred aspect, the polymerisation takes place in the presence of a chain transfer reagent.

Preferably, the chain transfer reagents have an acidic proton in the alpha position to a carbonyl group and are of the formula Z-CH_2-C(=O)-R", wherein R" is H, alkyl or aryl, and Z is selected from aryl, alkyl, H, amino, alkylamino, acyl, alkoxy (OR), thiol (SR) or heterocycle, where R is a hydrocarbyl group.

An example of a chain transfer reagent in which Z is aryl is 2',4',6'-trimethylacetophenone. Examples of chain transfer reagents in which Z is alkylamino include amino methyl ketones and amino ethyl ketones. An example of a chain transfer reagent in which Z is acyl is 2,4-pentanedione, i.e. Z is C(=O)CH_3 and R" is CH_3.

Other suitable chain transfer reagents are known in the literature and will be apparent to the person skilled in the relevant art.

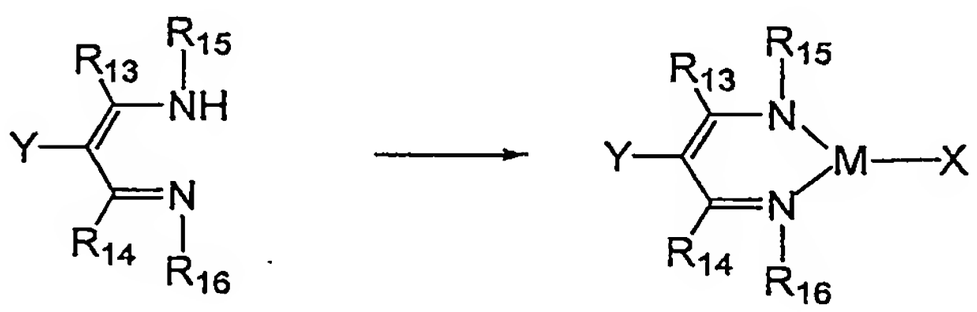
Preferably, the ratio of monomer to the complex in the above process is between 10:1 to 10^6:1.

A fourth aspect of the invention provides an article prepared by the above-described process.

A fifth aspect of the invention provides a composition comprising an acrylate and/or an alkylacrylate monomer and a complex of formula Ia as defined above.

A sixth aspect of the invention provides a composition comprising poly(alkylacrylate) and/or poly(alkylmethacrylate) or co-polymers thereof, and a complex of formula Ia as defined above.

A seventh aspect of the invention relates to a process for preparing a complex of formula II as defined hereinabove, where X is alkyl, said process comprising reacting a compound of formula IX with (a) ^{n}BuLi, and (b) XMgCl



IX II

Alternatively, in an eighth aspect of the invention, the complex of formula II may be prepared by reacting a compound of formula IX with a di(alkyl)magnesium compound, MgX_2.

In a ninth aspect, the invention provides a process for preparing a complex of formula II, as defined above, where X is an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, said

process comprising reacting the product obtained from the above-described seventh and eighth aspects with a compound of formula $HR^{10}R^{11}C\text{-}C(O)R^{12}$.

A tenth aspect of the invention provides a method for producing poly(alkylacrylate) or poly(alkylmethacrylate) having a syndiotacticity of greater than 75%, and preferably greater than 85%, said method comprising contacting the corresponding monomer (alkyl acrylate, or alkylmethacrylate, or mixtures thereof) with a complex of formula Ia as defined above in a suitable solvent.

Preferably, said method is carried out at a temperature in excess of -40°C.

Thus, in one particularly preferred embodiment, the complex of the invention is capable of affording polymethylmethacrylate with greater than 90% syndiotacticity in a highly controlled manner at a temperature in excess of -40°C.

The invention is further described by way of example and with reference to the following figures wherein:

Figure 1 shows the X-ray crystal structure for the compound $[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$.

Figure 2 shows a graph to illustrate the relationship between monomer conversion and M_n as determined by GPC (polydispersities, M_w/M_n, quoted in brackets).

Examples

Synthesis of $\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)_2\}Mg^{i}Pr$

$H_2C(C(CH_3)=N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)_2$ (6.880g, 1.64 x 10^{-2}mol) was dissolved in 50cm^3 toluene and lithiated via the addition of 6.7cm^3 ^{n}BuLi (2.5M in hexane, 1.68 x 10^{-2}mol). In a separate vessel 8.4cm^3 ^{i}PrMgCl (2.0M in Et_2O, 1.68 x 10^{-2}mol) was diluted with 10cm^3 toluene and concentrated under reduced pressure to a white viscous liquid. This procedure was repeated in order to remove most of the Et_2O from the Grignard reagent to avoid formation of $[\{HC(C(CH_3)=N\text{-}2,6\text{-}$

$^{i}Pr_2C_6H_3)_2\}Mg^{i}Pr\bullet Et_2O]$. The white sticky oil thus obtained was suspended in $20cm^3$ toluene and this mixture was then added dropwise to the solution of $\{HC(C(CH_3)=N\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2\}Li$ to afford a pale yellow, cloudy suspension.

The reaction was stirred overnight (18hours) at room temperature and then filtered. Volatiles were removed in vacuo and the resultant cream coloured solid was washed with $5cm^3$ cold (-78°C) n-pentane to afford 7.732g of a slightly off-white powder (1.59×10^{-2}mol, 97.0%).

^1H NMR (C_6D_6): δ 7.10 (m; 6H, *m-H*, *p-H*), 4.92 (s, 1H, $HC\{C(CH_3)NAr\}_2$), 3.13 (sept, 4H, $^3J_{HH}$ = 6.9Hz, $CHMe_2$), 1.67 (s, 6H, $HC\{C(CH_3)NAr\}_2$), 1.26 (d, 12H, $^3J_{HH}$ = 6.9Hz, $CH(CH_3)_2$), 1.14 (d, 12H, $^3J_{HH}$ = 6.9Hz, $CH(CH_3)_2$), 0.86 (d, 6H, $^3J_{HH}$ = 6.6Hz, $MgCH(CH_3)_2$), 0.13 (sept, 1H, $^3J_{HH}$ = 6.3Hz, $MgCH(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 168.84 ($HC\{C(CH_3)NAr\}_2$), 143.63 (C_{ipso}), 141.41 (C_{ortho}), 125.71 (C_{para}), 123.80 (C_{meta}), 94.89 ($HC\{C(CH_3)NAr\}_2$), 28.39 ($ArCH(CH_3)_2$), 24.10 ($HC\{C(CH_3)NAr\}_2$), 24.02 ($MgCH(CH_3)_2$), 23.15 ($ArCH(CH_3)_2$), 9.22 ($MgCH(CH_3)_2$). Elemental analysis for $C_{32}H_{48}N_2Mg$: C 79.24, H 9.97, N 5.78%. Found C 79.31, H 9.94, N 5.68%.

<u>Synthesis of $[\{HC(C(CH_3)=N\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$ (Ar = 2,4,6,-$Me_3C_6H_2$)</u>

0.8240g $\{HC(C(CH_3)=N\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2\}Mg^{i}Pr$ (1.70×10^{-3}mol) was suspended in $20cm^3$ toluene in a Schlenk tube placed in a solid CO_2 / acetone slush bath at -78°C. A $5cm^3$ toluene solution of 2',4',6'-trimethylacetophenone (0.2756g, 1.70×10^{-3}mol), also at -78°C, was then added dropwise over 5 minutes to afford a dark orange solution. On warming to ambient temperature the solution becomes increasingly pale yellow.

The reaction was stirred at room temperature for 18 hours. Removal of volatiles from the pale yellow-green solution gave a white solid which was then washed with $10cm^3$ cold heptane (-78°C). A saturated solution was then prepared by stirring the residual white powder in $15cm^3$ heptane at 60°C for 30 minutes. The solution was filtered and

allowed to slowly cool to yield very pale yellow rhomboid crystals of X-ray diffraction quality.

A second crop was prepared by reducing the volume of the mother liquor to approximately two-thirds and storing overnight in a freezer at -10°C.
Total yield: 0.673g, 5.58 x 10^{-4}mol, 65.7%

Synthesis of [{HC(C(CH_3)=N-2,6-$^{i}Pr_2C_6H_3$)$_2$}Mg(OC(=CH2)Ar)•Et_2O] (Ar = 2,4,6,-$Me_3C_6H_2$)

A chilled (-78°C) 10cm^3 Et_2O solution of 2',4',6'-trimethylacetophenone (0.4156g, 2.56 x 10^{-3}mol) was added dropwise over 30 minutes to a 10cm^3 Et_2O solution of {HC(C(CH_3)=N-2,6-$^{i}Pr_2C_6H_3$)$_2$}Mg^{i}Pr (1.2315g, 2.54 x 10^{-3}mol) in a solid CO_2 / acetone slush bath at -78°C. The reaction was allowed to warm to room temperature to give a pale yellow coloured solution, which was then stirred for a further 18 hours. Volatiles were removed *in vacuo* to give a sticky, cream-coloured solid which was washed with 5cm^3 pentane at -78°C to yield 1.312g of a white powder (1.94 x 10^{-3}mol, 76.3%).

Typical polymerisation procedure for [{HC(C(CH_3)=N-2,6-$^{i}Pr_2C_6H_3$)$_2$}Mg(OC(=CH_2) Ar)]$_2$

0.0084g [{HC(C(CH_3)=N-2,6-$^{i}Pr_2C_6H_3$)$_2$}Mg(OC(=CH_2)Ar)]$_2$ (1.39 x 10^{-5}mol) was weighed out into a glass vial and dissolved in 5cm^3 toluene to afford a pale yellow solution. The solution was cooled to –30°C. Methyl methacrylate (0.4183g, 4.18 x 10^{-3}mol, 300 equivalents) was then weighed out and cooled to –30°C and added to the initiator solution. The mixture was stirred for 10 minutes, followed by termination of the polymerisation by addition of 25µl MeOH.

GPC analysis was performed on a small aliquot, which was removed and dried in vacuo. The remainder of the solution was added to a large excess (ca. 150cm^3) MeOH, and the precipitate was collected and dried. ^{1}H NMR analysis ($CDCl_3$) gave 92% rr, 8%rm, (mm triad undetected).

Typical polymerisation procedure for [{HC(C(CH_3)=N-2,6-$^i Pr_2C_6H_3$)$_2$}Mg(OC(=CH_2)Ar)•Et_2O]$_2$

An identical method to that described above was employed. No significant differences in the behaviour of the polymerisation using the etherate initiator were observed.

Typical polymerisation procedure for[{HC(C(CH_3)=N-2,6-$^i Pr_2C_6H_3$)$_2$})Mg^{i}Pr]

An identical method to the procedure outlined for [{HC(C(CH_3)=N-2,6-$^i Pr_2C_6H_3$)$_2$}Mg(OC(=CH_2)Ar)]$_2$ was used. Immediately upon addition of methyl methacrylate to the initiator solution a bright yellow colouration was observed, which quickly became pale yellow. This colour persisted through the remainder of the reaction, disappearing upon addition of MeOH.

Investigation into the relationship between conversion and molecular weight

Using a similar method to that described above, 0.0080g [{HC(C(CH_3)=N-2,6-$^i Pr_2C_6H_3$)$_2$}Mg(OC(=CH_2)Ar)]$_2$ (1.33 x 10^{-5}mol) was dissolved in 6cm^3 $CDCl_3$. To this solution at -30°C was added neat methyl methacrylate (0.5317g, 5.31 x 10-3mol, 400 equivalents). The reaction was stirred at -30°C and at set time periods (120, 240, 360 and 480 seconds), 0.35cm^3 aliquots were removed and immediately terminated by addition to 20µl MeOH.

Monomer conversion was calculated by diluting the samples with a further 0.35cm^3 $CDCl_3$ and integrating the ^{1}H NMR resonances of the OCH_3 signals of the monomer (δ3.71) versus the polymer (δ3.56). Volatiles were then removed in vacuo and the residue was dissolved in non-deuterated $CHCl_3$. Analysis of this solution by gel permeation chromatography afforded a correlation of M_n versus conversion (see Figure 2).

Block copolymerisation of n-butylmethacrylate (BMA) and methylmethacrylate (MMA)

0.0106g [{HC(C(CH_3)=N-2,6-$^i Pr_2C_6H_3$)$_2$}Mg(OC(=CH_2)Ar)]$_2$ (1.76 x 10^{-5}mol) was dissolved in 3cm^3 $CDCl_3$ at -30°C. To this stirring solution was added 0.2526g BMA

(1.78 x 10^{-5}mol, 101 equivalents). After 10 minutes a 300µl aliquot was removed and terminated by addition to 10µl MeOH. The polymerisation was allowed to stir for a further 60 seconds and then 0.1756g MMA (1.75 x 10^{-5}mol, 100 equivalents) was added. The reaction was stirred for a further 10 minutes and terminated by addition of 25µl MeOH. ^{1}H NMR on the aliquot revealed that before the addition of the second monomer the BMA had been totally consumed.

GPC on the aliquot before addition of the MMA showed a single, monodisperse peak (Mn calc = 14,400, Mn obs = 13,800, Mw/Mn = 1.12). GPC on the block copolymer demonstrated Mn increased upon the incorporation of the MMA (Mn calc = 24,400, Mn obs = 22,800, Mw/Mn = 1.50).

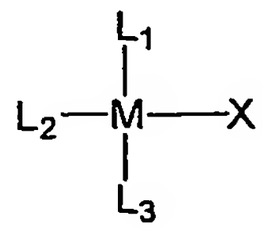
The use of 2',4',6'-trimethylacetophenone as a chain transfer agent

To a 3cm^3 $CDCl_3$ solution of [{HC(C(CH_3)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}Mg(OC(=CH_2)Ar)]$_2$ (0.0130g, 2.16 x 10^{-5}mol) at -30°C was added 17.9µl 2',4',6'-trimethylacetophenone (1.08 x 10^{-4}mol, 5.0 equivalents) to afford a bright yellow solution. 0.8675g MMA (8.66 x 10^{-5}mol, 402 equivalents) was then added. After 30 minutes the reaction was terminated by the addition of 25µl MeOH. GPC Mn calc (assuming maximum chain transfer) = 6,700; Mn obs = 7,200, Mw/Mn = 2.83).

Various modifications and variations of the described methods of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.

CLAIMS

1. A complex of formula I



I

wherein

M is Ca, Mg, Ba or Sr;

L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P and substituted or unsubstituted cyclopentadienide, where R^{1-6} are each independently H or hydrocarbyl;

L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C{=}NR^9$, $PR^7R^8R^9$, or a heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3 may be the same or different to L_2; or L_3 is linked to a further metal centre; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, an aryl group, an aryloxide or an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl;

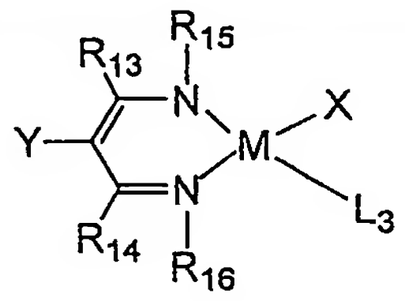
with the proviso that when L_1 and L_2 are $\{HC(C(CH_3){=}N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}$ and M is magnesium, X is other than Me or ^{t}Bu.

2. A complex according to claim 1 wherein R^1 and R^2 are hydrocarbyl, and R^{3-6} are H or hydrocarbyl.

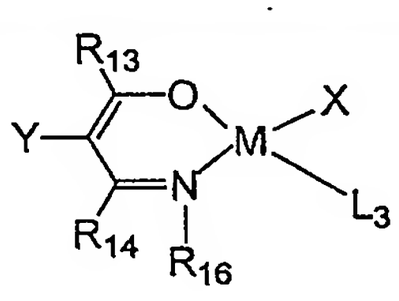
3. A complex according to claim 1 wherein R^1 and R^2 are each independently selected from branched or unbranched alkyl, branched or unbranched alkenyl, or aryl, each of which may be substituted or unsubstituted.

4. A complex according to claim 1 wherein L_1 and L_2 are linked to form a bidentate ligand selected from a beta-diketiminate and a beta-ketoiminate.

5. A complex according to claim 4 of formula II or III



II



III

wherein

Y is H, hydrocarbyl or CN;

R^{13-16} are each independently selected from H and hydrocarbyl; or Y and R^{13} are linked to form a hydrocarbyl group; and

L_3 is as defined in claim 1.

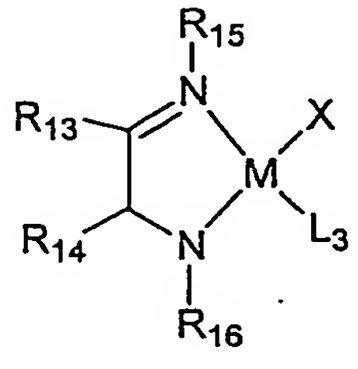
6. A complex according to claim 5 wherein

Y is selected from H, CN, alkyl, aryl, haloalkyl or heteroalkyl;

R^{13-16} are each independently selected from alkyl, aryl, heteroalkyl, haloalkyl, cycloalkyl and a heterocyclic ring containing at least one O, N or S atom; or Y and R^{13} are linked to form an aryl group; and

L_3 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7C{=}NR^8$, $PR^7R^8R^9$, thiophene and tetrahydrofuran, where R^{7-9} are each independently H or a hydrocarbyl group.

7. A complex according to claim 1 of formula V



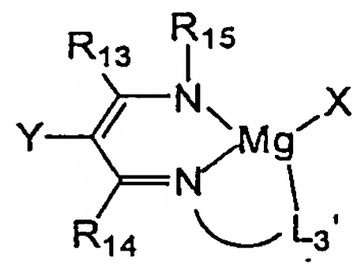
V

wherein R^{13-16} are as defined in claim 5 or claim 6, and where R^{13} and R^{15} are optionally linked to form an aryl group.

8. A complex according to any one of claims 1 to 3 wherein L_1, L_2 and L_3 are linked to form a tridentate ligand.

9. A complex according to claim 8 wherein L_1, L_2 and L_3 are linked to form a tridentate ligand selected from a beta-diketiminate with a pendant donor group, and a Schiff base derivative with a pendant donor arm.

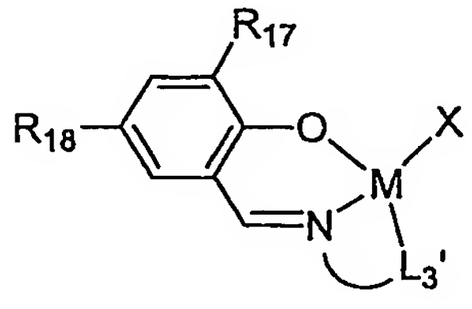
10. A complex according to claim 9 of formula VI



VI

wherein L_3' is defined as for L_3 in claim 1, and is linked to the nitrogen of the bidentate ligand via a linker group.

11. A complex according to claim 9 wherein said complex is of formula VII

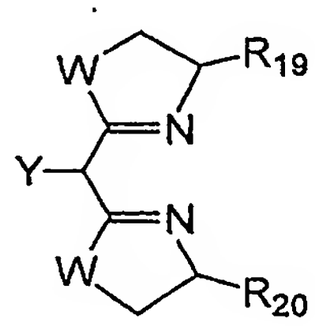


VII

wherein L_3' is defined as for L_3 in claim 1, and is linked to the nitrogen of the bidentate ligand via a linker group, and R^{17-18} are as defined for R^{13-16} above .

12. A complex according to claim 10 or claim 11 wherein the linker group is $(CH_2)_n$ where n is 0-6, an arylene group, or SiR_2, where R is hydrocarbyl.

13. A complex according to claim 1 wherein L_1 and L_2 form a bidentate ligand of formula VIII



VIII

wherein

Y is as defined above;

W is O, NH, NR' or CH_2 where R' is hydrocarbyl; and

R^{19-20} are as defined for R^{13-16} above.

14. A complex comprising a dimer of a complex according to any preceding claim.

15. A complex according to claim 1 selected from the following:

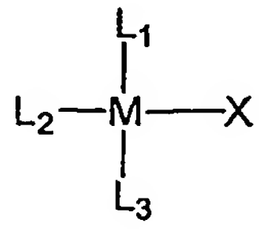
$\{HC(C(CH_3)=N\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2\}Mg^{i}Pr$;

[{HC(C(CH_3)=N-2,6-$^{i}Pr_2C_6H_3$)$_2$}Mg(OC(=CH_2)Ar)]$_2$;

[{HC(C(CH_3)=N-2,6-$^{i}Pr_2C_6H_3$)$_2$}Mg(OC(=CH2)Ar)•Et_2O];

wherein Ar = 2,4,6,-$Me_3C_6H_2$.

16. Use of a complex of formula Ia as a polymerisation initiator,



Ia

wherein

M is Ca, Mg, Ba or Sr;

L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P and substituted or unsubstituted cyclopentadienide, where R^{1-6} are each independently H or hydrocarbyl;

L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C=NR^9$, $PR^7R^8R^9$, or a heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3 may be the same or different to L_2; or L_3 is linked to a further metal centre; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, and aryl group, an amide, an alkoxide, an aryloxide or an enolate group of formula $R^{10}R^{11}C=CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl;

with the proviso that when L_1 and L_2 are {HC(C(CH_3)=N-2,6-$^{i}Pr_2C_6H_3$)$_2$}, M is magnesium, X is other than Me or ^{t}Bu.

17. Use according to claim 16 in the polymerisation of acrylate and/or alkyl acrylate monomers.

18. Use according to claim 16 or 17 which further comprises the use of a chain transfer reagent.

19. A process for the polymerisation of acrylate and/or alkylacrylate monomers, said process comprising contacting an initiating amount of a complex of formula Ia as defined in claim 16 with an acrylate and/or an alkylacrylate monomer in the presence of a suitable solvent.

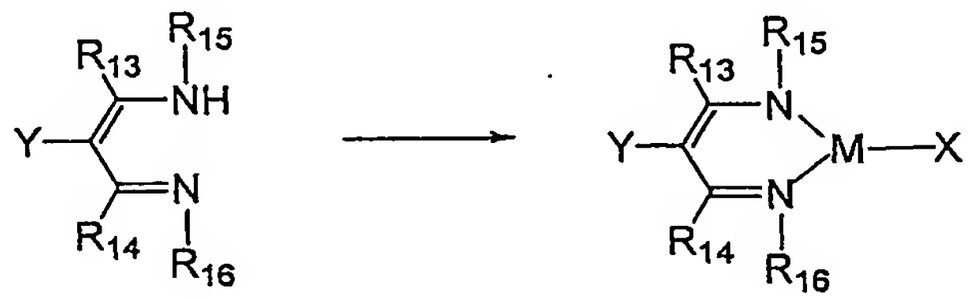
20. A process according to claim 19 wherein the ratio of monomer to the complex is between 10:1 and 10^6:1.

21. An article prepared by a process according to claims 19 or 20.

22. A composition comprising an acrylate and/or an alkylacrylate monomer and a complex of formula Ia as defined in claim 16.

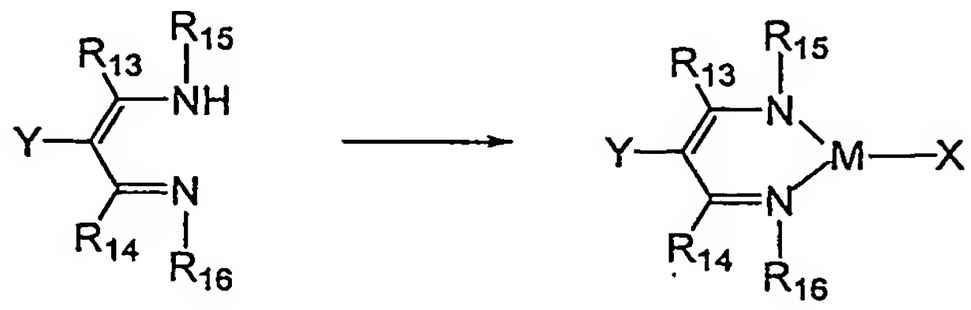
23. A composition comprising poly(alkylacrylate) and poly(alkylmethacrylate) or copolymers thereof, and a complex of formula Ia as defined in claim 16.

24. A process for preparing a complex of formula II as defined in claim 5, where X is alkyl, said process comprising reacting a compound of formula IX with (a) ^{n}BuLi, and (b) XMgCl



IX II

25. A process for preparing a complex of formula II as defined in claim 5, where X is alkyl, said process comprising reacting a compound of formula IX with MgX_2



IX II

26. A process for preparing a complex of formula II, as defined in claim 5, where X is an enolate group of formula $R^{10}R^{11}C=CR^{12}O$-, said process comprising reacting the product obtained from the process of claim 24 or claim 25 with a compound of formula $HR^{10}R^{11}C$-$C(O)R^{12}$.

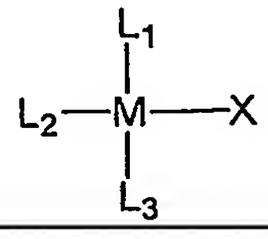
27. A method for producing polymethacrylate having greater than 75% syndiotacticity, said method comprising contacting methacrylate monomer with a complex of formula Ia as defined in claim 16 in the presence of a suitable solvent.

28. A method according to claim 27 which is carried out at a temperature in excess of -40°C.

ABSTRACT

COORDINATION COMPLEX

The present invention provides a complex of formula I



I

wherein

M is Ca, Mg, Ba or Sr;

L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P and substituted or unsubstituted cyclopentadienide, where R^{1-6} are each independently H or hydrocarbyl;

L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C{=}NR^9$, $PR^7R^8R^9$, or a heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3 may be the same or different to L_2; or L_3 is linked to a further metal centre; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, an aryl group, an aryloxide or an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl;

with the proviso that when L_1 and L_2 are $\{HC(C(CH_3){=}N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)_2\}$ and M is magnesium, X is other than Me or ^{t}Bu.

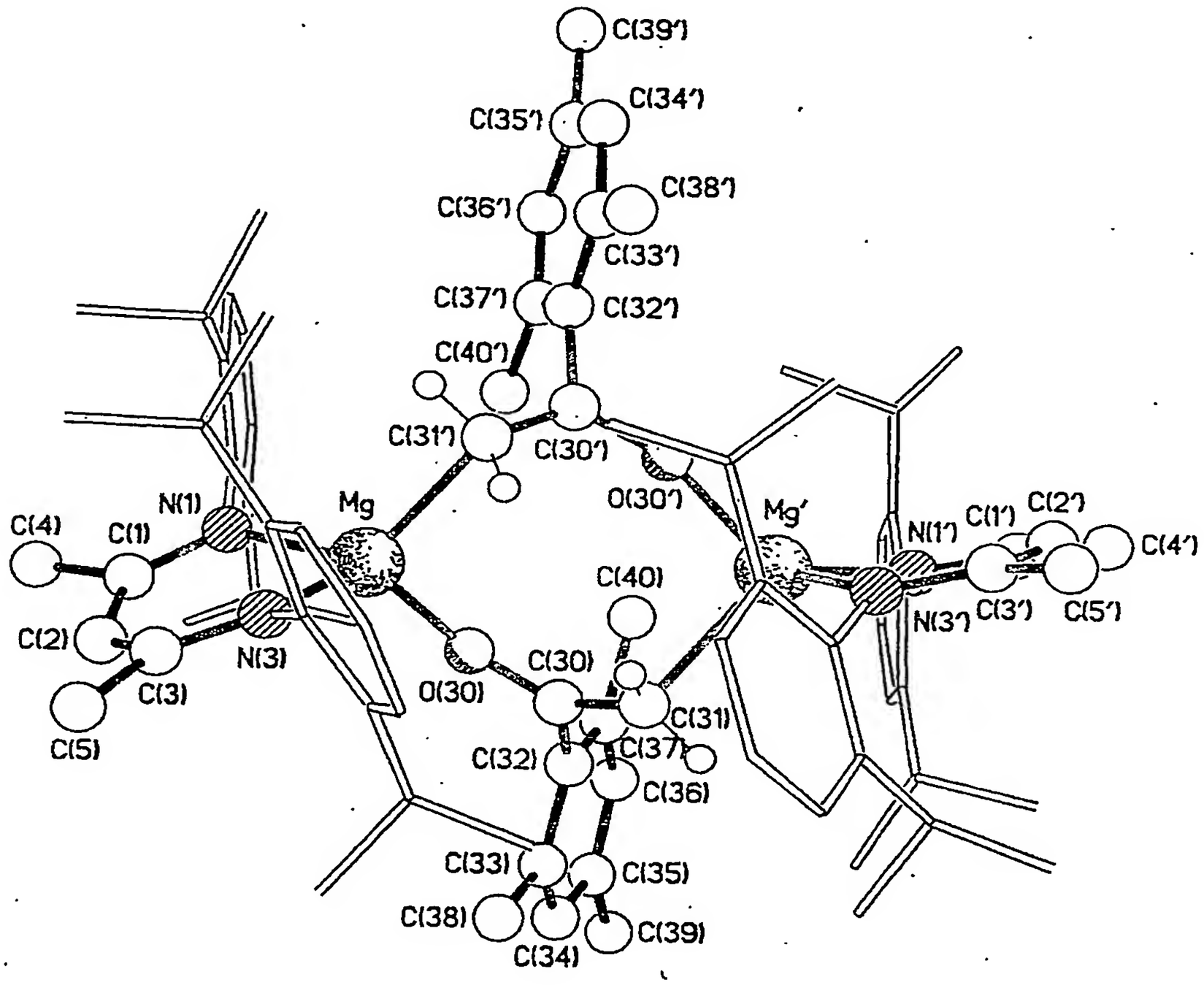

C(39')
C(34')
C(35')
C(38')
C(36')
C(33')
C(37')
C(32')
C(40')
C(31')
C(30')
O(30')
Mg'
N(1')
C(1')
C(2')
C(4')
N(3')
C(3')
C(5')
N(1)
Mg
C(4)
C(1)
C(40)
C(2)
N(3)
C(30)
O(30)
C(3)
C(31)
C(5)
C(32)
C(37)
C(36)
C(33)
C(35)
C(38)
C(39)
C(34)

FIGURE 1

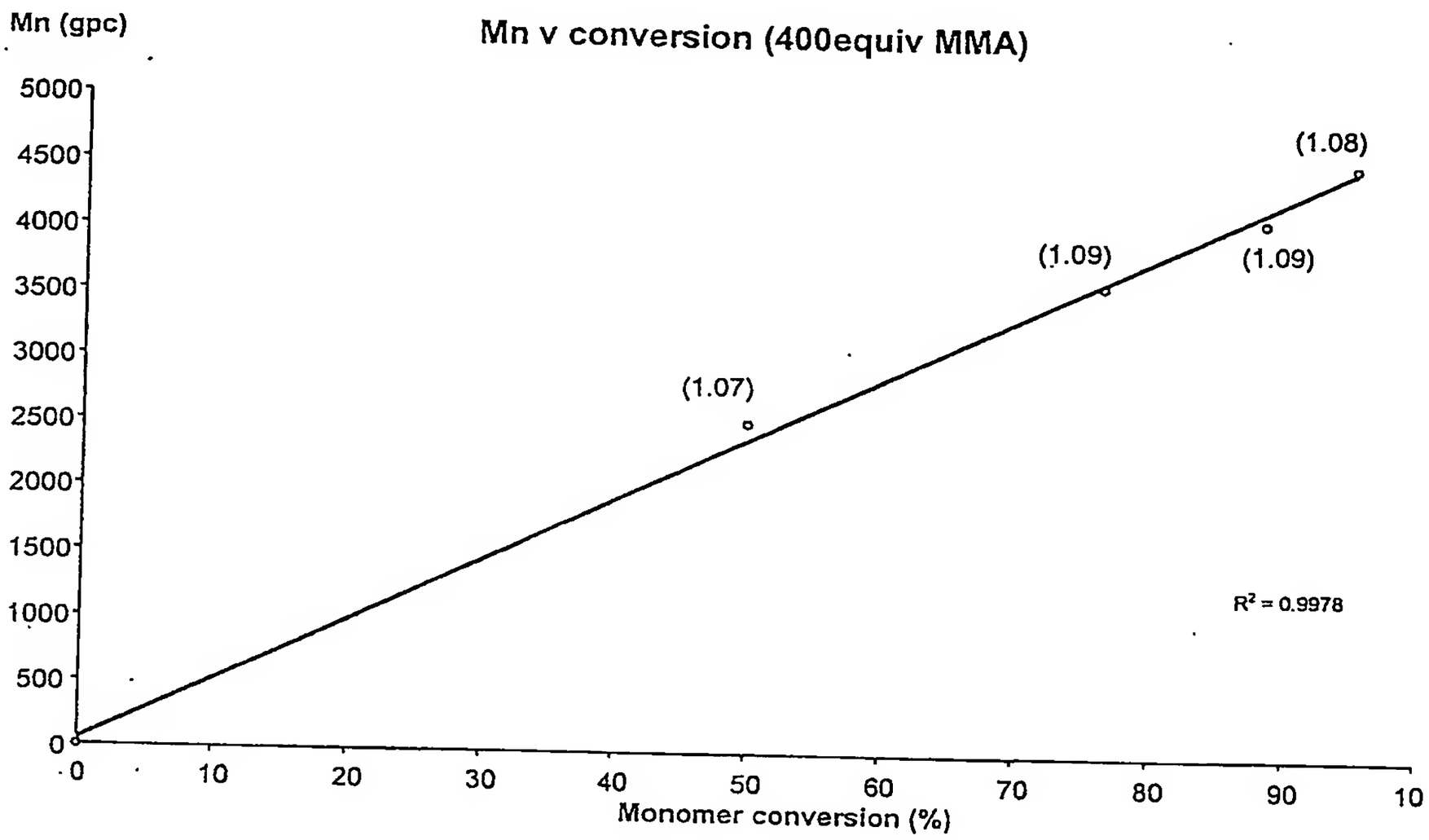

Mn v conversion (400equiv MMA)
Mn (gpc)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
80
90
10
Monomer conversion (%)
(1.08)
(1.09)
(1.09)
(1.07)
R² = 0.9978

FIGURE 2